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ANALYSIS OF MC2730 CLEANING PROCEDURES AS RELATED TO ANOMALOUS VOLTAGE DEGRADATION

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Electrical [illegible]

the [illegible] Radioisotope [illegible] a study of the cause [illegible] procedures used to clean the thermo[illegible] retained electrically [illegible] microprobe analysis, a surface [illegible] layer was [illegible] carbon layer resulted [illegible] Chemical, UV and plasma cleaning [illegible] studied [illegible] determine their effectiveness in removing [illegible] from [illegible] samples. The most effective [illegible] a combination of chemical and UV cleaning. This [illegible] was shown to be far more effective than chemical cleaning by itself and was able to reduce the carbon levels to levels which were nearly non-detectable by Auger electron spectroscopy (AES).

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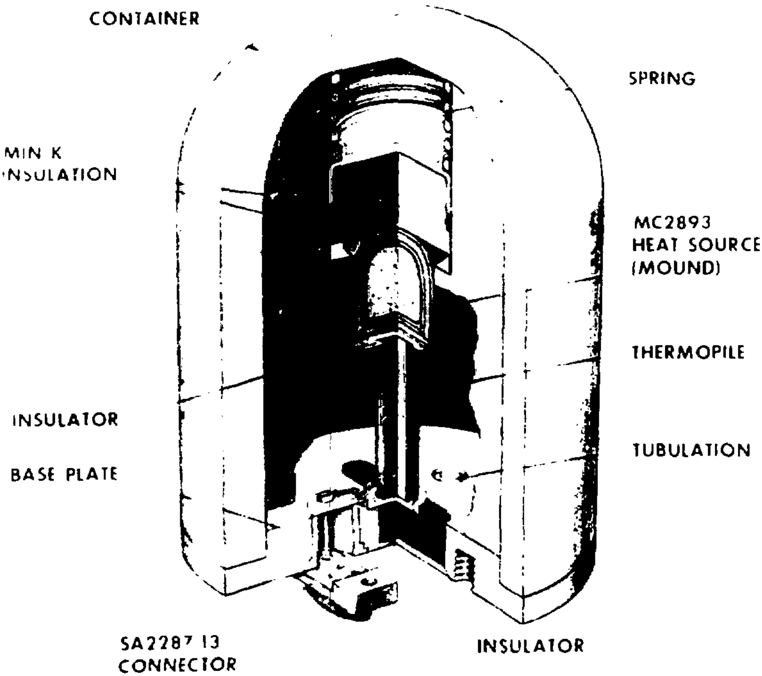
INTRODUCTION

The RTG [illegible] is a [illegible] Thermoelectric [illegible] designed and [illegible] by Sandia Laboratories [illegible]. A schematic diagram of the various components [illegible]. During operation a Pu^{238} [illegible] source (MC2[illegible]) [illegible] sufficient heat to [illegible] to maintain a temperature difference of [illegible]. The thermopile consists of two [illegible] which channels fabricated from [illegible] SiGe [illegible]. The two channels are electrically connected in series. [illegible] connections between the individual SiGe elements are [illegible] electrodes. The thermopile is electrically [illegible] but thermally connected to both the heat source and [illegible] by boron nitride disks. The heat source and thermopile are thermally isolated from the outside environment by [illegible] insulation (Min-K) which is very hygroscopic and [illegible] out in vacuum. The whole unit must be assembled in a dry box atmosphere.

Some of the RTG's produced at GEND have exhibited an anomalously large decrease in output voltage as a function of time. Electrical tests by W. R. Abel, 2531, indicated that shorts were developing between the two channels of the unit at the hot end. Optical examination by 2531 indicated numerous areas of contamination on the ends of the thermopile. One suspected source of the contamination was photoresist (which



MC2730

rtg

[illegible] 30 radioisotopic thermo-electric [illegible].

is used in the W contact definition) that had not been completely removed during cleaning.

As part of the overall effort to determine the cause of the anomalous degradation, Division 5823 was asked to provide surface analysis support in an attempt to identify the material causing the short and to evaluate the effectiveness of alternate procedures for removing photoresist. This report details the investigations which led to the identification of the cause of the electrical degradation. In addition, an alternate cleaning procedure for removing photoresist is suggested.

EXPERIMENTAL RESULTS

Contamination on Thermopiles

The ends of a number of thermopiles removed from [illegible] units were examined using a scanning Auger microprobe with a minimum beam diameter of 2 μm. With this instrument both secondary electron images and scanning Auger images could be obtained. A typical example of a secondary electron image is shown in Figure 2. In addition to the W, SiGe, and glass areas, two other features are seen. The first is a rather large number of particles. Auger analysis of these particles indicates that they are high in Si and O. They probably originate from the Min-K insulation which is a fine particle silica. Also seen in this picture are a number of dark lines which run roughly perpendicular to the glass interface which separates the two channels of the thermopile. When observed at lower magnification, these lines appear circular. Analyses of these areas indicate that they are high in B and N and probably originate

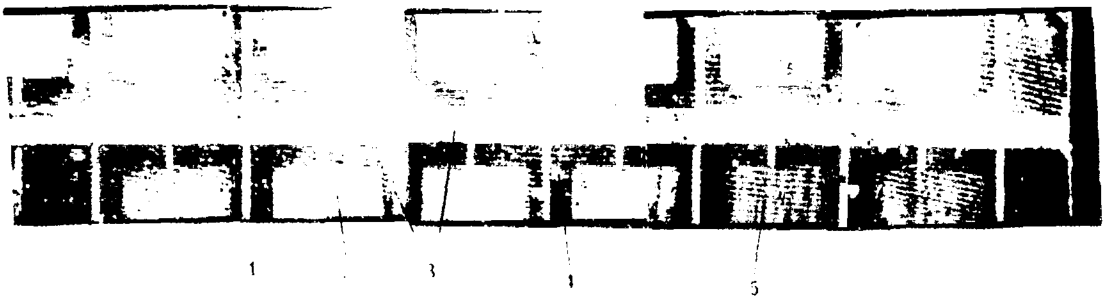


Figure 2. Scanning electron micrograph of the end of a thermopile removed from a failed RTG. In addition to the SiGe (1), W (2) and glass layers (3), a large number of particles (4) and circular striations (5) are observed.

from the machining marks on the BN used for the electrical isolation. Analyses of the W and SiGe areas indicate the presence of C, O, Cl, Na. The glass area has varying amounts of C, O, and Si. Figure 3 shows a SEM and C (KLL) Auger map of the hot end of a thermopile which had been identified to have an electrical short near the edge (right side) of the pile. As can be seen from the Auger map, carbon is observed on the W pads. The very bright spots between the pads are due to electrical charging of insulating particles (mostly from the Min-K). The bright area near the righthand side along the glass layer is not due to charging and indicates a high level of carbon is present in this area. The high level of C is also observed "around the corner" on the glass layer on the side of the thermopile and extends approximately 4 mm down the thermopile. This observation led to the hypothesis that the cleaning procedure used to remove the photoresist was insufficient, especially near the edge of the pile. It was speculated that at high temperature the photoresist was charring and becoming conducting. This speculation was supported by electrical conductivity measurements made by R. Johnson, 5815, on the photoresist.[2] The electrical resistance between the two channels of the degraded thermopile, shown in Figure 3, was determined by organization 2531 to be 10,000 ohms. This area was sputter cleaned in the Auger system using 5 keV Ar ions. After sputtering, the photographs shown in Figure 4 were obtained. These data indicate that the C contamination was almost eliminated by the sputtering. Subsequent electrical

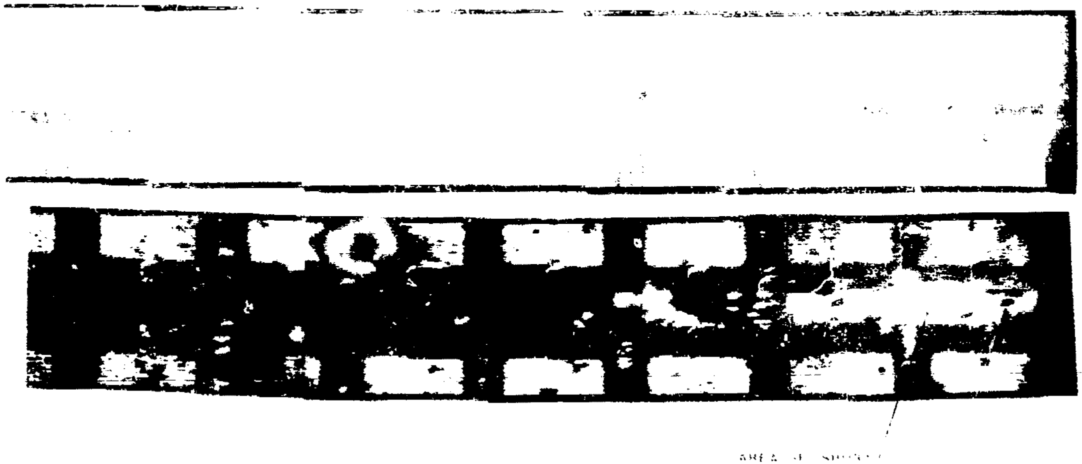


Figure 3. Scanning electron micrograph and carbon Auger map of the hot end of a thermopile removed from a failed RTG. A short in this unit had been electrically isolated to the glass area in the right hand portion of the photograph. Note the high carbon observed in this area.

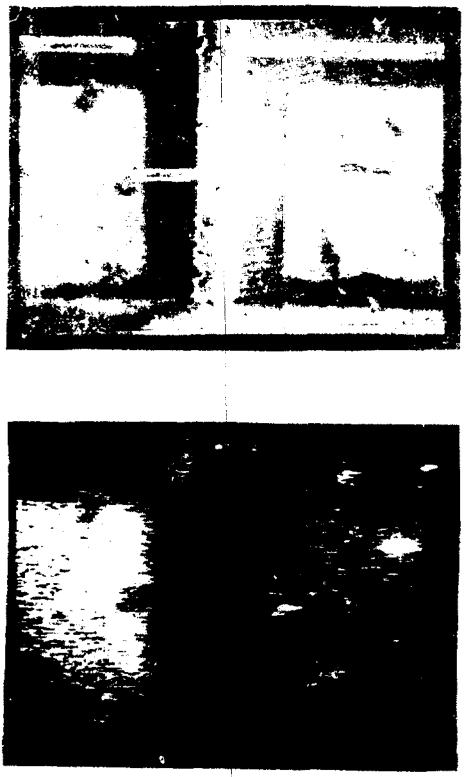


Figure 4. Scanning electron micrograph and carbon Auger map obtained after sputter clearing the high carbon area shown in previous figure. Note the low level of the remaining carbon.

measurements indicated that the resistance increased by three to four orders of magnitude to a value which was in the acceptable range. From these data it was concluded that carbon was a major contributor to the shorting problem and that the problem was one of surface contamination (i.e., the removal of a few hundred Å of material corrected the problem). These data did not, however, identify the source of the carbon. Because removal of photoresist was known to be a problem and the electrical tests of R. Johnson indicated that at elevated temperatures photoresist could give the anomalously high conductivities which had been measured on thermopiles, tests were conducted on the effectiveness of various cleaning procedures in removing the photoresist.

Cleaning Procedures

Auger analysis was used to evaluate methods for removing photoresist from the thermopiles. The cleaning procedures which were tested consisted of three general groups or combinations of groups. These were chemical, ultraviolet, and plasma cleaning (both oxygen and hydrogen). Plasma and ultraviolet cleaning were included because they have been shown in the past to be very effective in removing hydrocarbon contamination.

There are a number of reports in the literature where ultraviolet radiation has been used to remove hydrocarbons.[3] The principle mechanism for this reaction is believed to be the formation of ozone which then reacts with the hydrocarbon to form volatile products. Because this reaction is rather slow, it is usually used as a "final step" in the cleaning process.

This is also the way it was used for these measurements. In collaboration with F. W. Oswalt of 5821, three chemical cleaning procedures were evaluated. These are listed in Table I. The first was similar to GEND's method which included scrubbing with cotton swabs. The second was a procedure which was suggested by Frank Oswalt and the third was Frank Oswalt's procedure followed UV cleaning. The effectiveness of these cleaning procedures was determined by monitoring the carbon and Si Auger signals from Si samples which had been coated with photoresist and cleaned by the various methods. The results are shown in Figure 5. These data indicate that scrubbing is not as effective as multiple stages of ultrasonic cleaning and that the addition of UV as a final step in the cleaning process plays a major role in reducing the carbon level at its lowest value. It should be noted that the thermopiles can be stored in a UV chamber after cleaning and their recontamination can be prevented.

A thermopile was cleaned by the above method and the SEM results are shown in Figure 6. As can be seen, the particulate and stain levels are very low. In addition, surface analysis of the various areas indicates that the carbon contamination level is also low indicating that with this procedure, thermopiles can be successfully cleaned prior to assembly.

To qualify UV for the cleaning process the question of oxidation of the W contacts and subsequent loss of adhesion had to be addressed. This was studied by UV-treating W thin films for varying periods of time and then determining the oxygen concentration as a function of depth. The results of

TABLE I

Methods Which Were Tested for Their Effectiveness in Removing Photoresist

Method I	Method II	Method III
1. Scrubbing with cotton swabs with 1, 1, 1, tri-chloroethane	Ultrasonic cleaning for 2 min followed by blow off with effaduster	Same as Method II followed by 24 hr expo-sure to [illegible]
2. Ultrasonic cleaning in 1, 1, 1 trichloroethane (2 min)	1. Trichloroethylene	
3. Ultrasonic cleaning in isopropyl alcohol (2 min)	2. Isopropyl alcohol	
4. Blow off with effa-duster	3. Deionized water	
	4. Isopropyl alcohol	
	5. Isopropyl alcohol	

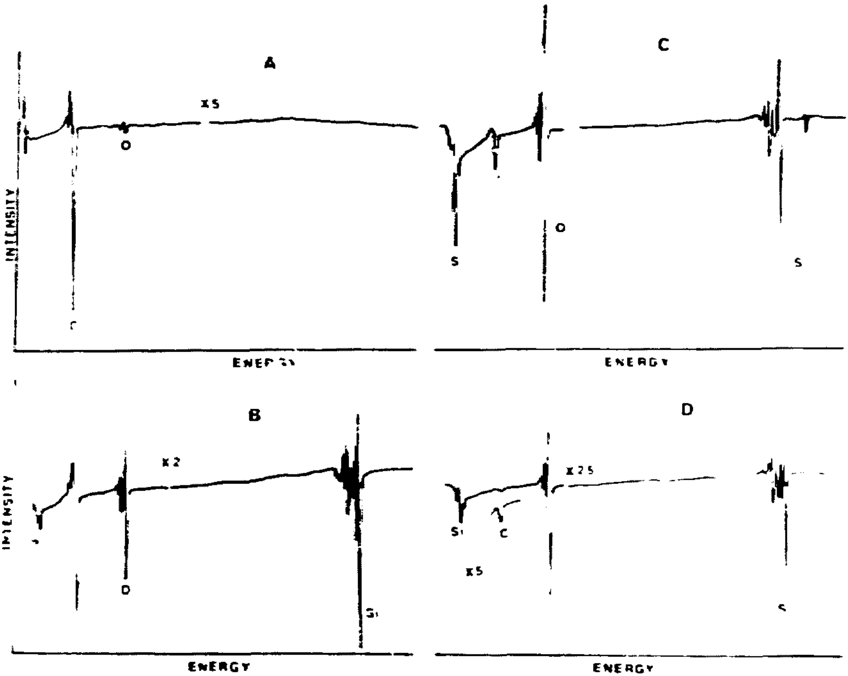


Figure 5. Auger spectra obtained from Si samples coated with photoresist after A) no cleaning, B) Method I (Table I), C) Method II, and D) Method III.

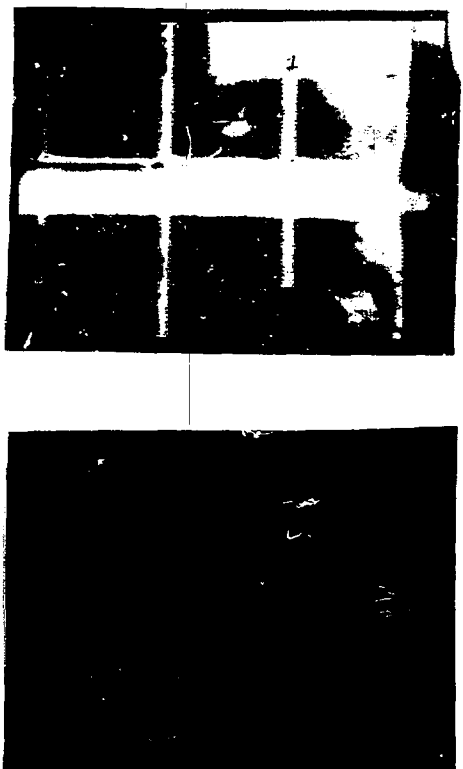


Figure 6. Scanning electron micrograph and carbon Auger map of a thermopile after cleaning by method III. Note the low level of particles and carbon.

the measurement are shown in Figure 7. As this figure indicates, the depth to which the oxygen extends is independent of the sample treatment time (the oxygen level in the surface layer may change, however). The depth to which the oxygen extends is a small fraction of the total W thickness and therefore the UV treatment should not degrade the quality of the W contacts.

The rate at which photoresist can be removed in a "dry" process can be increased significantly by using an oxygen plasma rather than UV. As a demonstration of the effectiveness of oxygen plasma cleaning, photoresist was removed from a W film by oxygen plasma alone. Figure 8 shows a comparison of the x-ray photoelectron spectra (XPS) taken before cleaning (primarily C and O) and after cleaning at 100 watts at [illegible] Torr oxygen for 15 min (very little carbon along with W, O and Sn). These data indicate that the oxygen plasma is very efficient in removing the hydrocarbon (to a level as low as that obtained by any other method). However, a significant quantity of tin was being deposited during the treatment. Data obtained by secondary ion mass spectroscopy indicated that the Sn was in an oxidized state. Bulk analysis by emission spectroscopy indicated that the photoresist (Kodak Metal Etch Resist) contained approximately 0.3 wt. Sn in the bulk. This value is much lower than that observed on the surface. Apparently during the plasma treatment the hydrocarbon portion of the photoresist is removed and the Sn from the bulk is concentrated in a surface layer on the sample. While this negates the use of oxygen plasma alone as a one step "dry" method for removing photoresist,

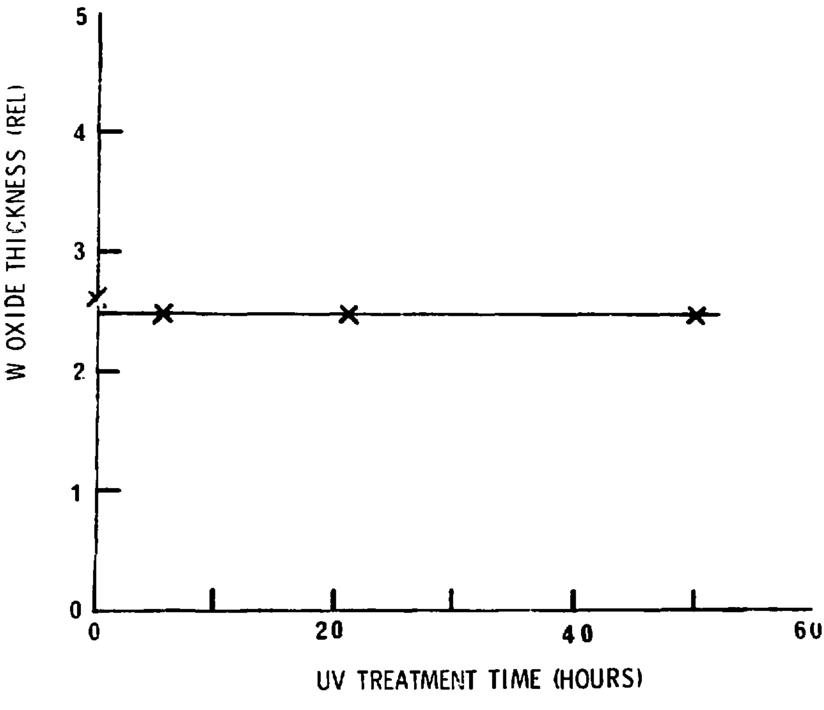


Figure 7. Plot of the depth (sputter time) oxygen extends into a W film as a function of UV treatment time.

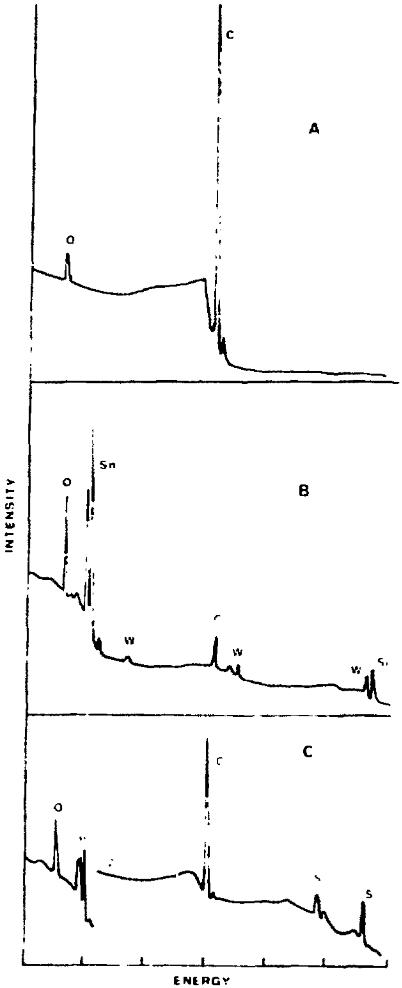


Figure 8. X-ray photoelectron spectra obtained from W films coated with photoresist after A) no cleaning, B) 15 minutes of oxygen plasma and C) 24 hours of hydrogen plasma.

it may be useful for other photoresists which do not contain inorganic constituents. This problem could be alleviated by combining it with chemical cleaning as was used in the UV case. However, it was felt that the total effectiveness would not be greater than the UV and the simplicity of the UV system over a plasma system favored the UV.

An alternate possible means of removing the photoresist is the use of a hydrogen plasma. Previous work with graphite indicated that a hydrogen plasma would aggressively attack carbon to form volatile hydrocarbons (primarily methane). Photoresist samples on W were exposed to hydrogen plasma which had the same pressure, power as that used for the oxygen plasma. Visual observation indicated that the photoresist had not been removed by the plasma. XPS and SIMS confirmed this observation, i.e., a large C signal was detected. In addition, Si was detected after the plasma treatment. The Si is due to a reaction of the hydrogen plasma with the quartz reaction chamber to form silane and a subsequent deposition of the silane onto the sample. This effect has been observed in other studies where metals have been treated in a hydrogen plasma. From these results it was concluded that a hydrogen plasma is not effective in removing the Kodak Metal Etch Resist.

The detection of Sn in the photoresist led to reexamination of the data obtained from the shorted area on the thermopile in order to determine if Sn was present in this area. If Sn could be found, it would be a positive indication that photoresist was the source of the carbon contamination. No signal from Sn was found in the Auger data. Because the bulk concentration of Sn in the photoresist is near the Auger detection limit, these findings did not completely rule out photoresist as the source of the carbon. They did suggest, however, that one should carefully examine all of the processing steps for the source of the carbon contamination. When this was done by organization 2531 and GEND personnel, it was found that the bakeout oven used to vacuum bake the thermal insulation (Min-K) was untrapped and that significant amounts of oil had backstreamed into the oven and were contaminating the Min-K. It was suspected that this contamination could be transferred to the thermopile and be the source of the carbon which was the cause of the shorting problem. When test units were built with Min-K which had been vacuum baked in a "clean" oven, the accelerated degradation of the units disappeared. Therefore the primary cause of the accelerated degradation is thought to have been oil contamination. However, thermopile cleaning is still considered to be a critical process and UV cleaning has been added to minimize contamination problems.

CONCLUSIONS

From these studies two major contributions were made to the understanding and reduction of the degradation of the MC2730. First, it was clearly shown by Auger analysis that the electrical degradation was caused by surface carbon contamination. The source of the carbon contamination was subsequently identified (by 2531 and GEND personnel) as pump oil contamination of the Min-K thermal insulation. Second, thermopile cleaning procedures were evaluated and an improved procedure which used UV cleaning as a final step was shown to be superior to the one used on the production line. When the pump oil contamination was eliminated and improved handling and cleaning procedures were incorporated into the production line, the MC2730 successfully passed TMS.

ACKNOWLEDGEMENTS

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